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THE FRAGMENTATION OF THE IONS OF NONAN-4-ONE:

A STUDY BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The fragmentation of the ions of the compound nonan-4-one were
studied in detail with low-energy collision-induced dissociation (CID)
in a triple quadrupole mass spectrometer. Ions of the sample molecule
created in an EI source are mass selected by a quadrupole mass filter,
dissociated by low-energy collision with neutral molecules in a quadru-
pole collision chamber, and the dissociation products are mass-selected

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by a second quadrupole mass analyzer. The normal EI mass spectrum of nonan-4-one shows 47 fragment ions. A fragmentation spectrum is obtained for each of the ions from the EI source. The result is the positive identification of over 400 parent-daughter pairs. This compares with a total of 47 observed pairs (37 confirmed) from all previous metastable ion studies. Normal alkanone fragmentations are observed: $\alpha$-cleavage, loss of CO or $C_2H_4$ from $\alpha$-cleavage ions, and McLafferty rearrangement in the long chain. The relative abundances of the short chain and long chain $\alpha$-cleavage fragments are demonstrated to depend on the fragmentation energy available with the long chain fragment predominating at lower energies.

The fragmentations observed are grouped for discussion. A number of parent-daughter structures and fragmentation mechanisms are confirmed and some new ones are proposed. New graphical representations of the fragmentation patterns have been devised to accommodate the large amount of information produced in this study.

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THE FRAGMENTATION OF THE IONS OF NONAN-4-ONE:
A STUDY BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

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The electron-impact induced fragmentation of aliphatic ketones has been
widely investigated (1).   The techniques which have been
utilized to help in these studies include metastable decomposition
studies (2-4), ion cyclotron resonance (ICR) (5), and the use of deuterium
labelled compounds (4-7).  The particular attention given to nonan-4-one
includes a study of the metastable ions observed from this compound with
an Ion Kinetic Energy (IKE) Spectrometer (7).  This paper describes a detailed
study of the fragmentation of this compound using low-energy collison-
induced dissociation (CID) of selected ions in a triple quadrupole mass
spectrometer.

Experimental

In selected ion fragmentation, several ion species are generated from
a sample, ions of a particular mass are selected for fragmentation, and the
resulting fragment ions are mass analyzed.  As the present study illustrates,
the use of two sequential stages of mass analysis with fragmentation occuring
between them makes it possible to determine the routes of formation and
fragmentation of ions in the mass spectrum.

We recently introduced the concept of performing selected ion  frag-
mentation with a triple quadrupole mass spectrometer (8).  The instrument
used in this study has been described (9).  It consists of, in series, a
dual chemical ionization/electron impact (CI/EI) ionization source, a quad-
rupole mass filter, an RF-only quadrupole that can be pressurized for CID,

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a second quadrupole mass filter, and an electron multiplier. Mass resolution
of one part in 1500 is possible over the entire mass range of 1-1000 amu.
The high efficiency of each component in the system allows fragmentation
processes of very low probability to be readily observed (9).

## Results and Discussion

Figure 1 displays all the collisional fragmentations observed in this
study (below the diagonal) and all the metastable transitions seen in the
IKES study (above the diagonal) (7). The EI mass spectrum of nonan-4-one
shows 47 fragment ions, and the metastable study indicates 37 confirmed and
7 unconfirmed metastable transitions. The triple quadrupole system shows
over 400 CID peaks, which include the 44 fragmentations observed in the
metastable data as well as a host of others. Not only does the triple
quadrupole system with CID produce a significant increase in the number of
fragmentations observed, it also provides direct mass analysis of both the
parent and daughter ions at unit mass resolution.

A combination of complementary methods was used in the IKES study of
metastable transitions (7). The kinetic energy loss upon metastable frag-
mentation results in broad peaks which make difficult the unambiguous mass
assignment of the parent and fragment ions (e.g. $142^+ \rightarrow 99^+$ or $142^+ \rightarrow 98^+$) in
IKES scans. (In these scans it is the ratio of parent ion mass/charge
squared to daughter ion mass/charge that is actually measured, so that
several pairs of parent/daughter ions (e.g. $142^+ \rightarrow 86^+$ and $71^+ \rightarrow 43^+$) may
contribute to a single peak). Comparison of IKE spectra of isotopically
labelled and unlabelled samples can help in the assignment of specific
transitions for each peak. In the high voltage scanning technique that was
also employed, mass losses of greater than 50% cannot be observed.

The major fragmentations observed in the CID studies are depicted in Figure 2. The stars indicate transitions that are also observed in the metastable studies (7). Redundant pathways are not shown (e.g., $142^+ \to 85^+$ is not shown since the transitions $142^+ \to 114^+$ and $114^+ \to 85^+$ do appear). Note that the CID data do not indicate any ions of m/z not seen in the EI mass spectrum; rather, they provide interconnections between these ions, specific fragmentation pathways for the production and further fragmentation of each ion.

The fragmentations normally attributed to alkanones are all observed: $\alpha$-cleavage ($142^+ \to 99^+$ and $142^+ \to 71^+$), loss of CO or $C_2H_4$ from the $\alpha$-cleavage ions ($99^+ \to 71^+$ and $71^+ \to 43^+$), McLafferty rearrangement in the long chain ($142^+ \to 86^+$), and the resultant double McLafferty rearrangement ($86^+ \to 58^+$). These transitions, also seen in the IKES study of metastables, account for the genesis of the five major fragment ions in the electron impact mass spectrum. These fragmentations also shed some light on the preferential $\alpha$-cleavage of the short or long chain. At high collision gas pressures ($1 \times 10^{-4}$ torr Argon), the long chain is preferentially eliminated, as is the case in 70eV EI spectra (1). At lower collision gas pressure ($2 \times 10^{-5}$ torr Argon), however, the short chain is preferentially lost, a feature that is also observed in 10eV EI spectra (10) and metastable studies (2). It has been postulated (10) that further decomposition of the ion resulting from $\alpha$-cleavage of the short chain is the cause of its reduced intensity in the 70 eV EI spectrum. Further fragmentations are minimized at 10eV, and therefore the short chain $\alpha$-cleavage ion remains the more intense. The CID data are in agreement with this rationalization, since multiple collisions and therefore further fragmentations are more likely at higher collision gas pressure. This rationale requires faster rates of decomposition and/or more pathways for the further decomposition of the ion which results from $\alpha$-cleavage of the short chain compared to that from the long chain loss.

That reasoning can be checked by comparing the degree of fragmentation in the CID spectra of the two $\alpha$-cleavage ions. The ion arising from $\alpha$-cleavage of the short chain ($99^+$) shows 97% fragmentation (only 3% of the ion current is due to $99^+$) at $1 \times 10^{-4}$ torr compared to only 88% fragmentation for the ion $71^+$ which arises from the $\alpha$-cleavage of the long chain. This higher probability for further fragmentation of $99^+$ compared to $71^+$ explains why $71^+$ predominates in cases where enough energy is available for further fragmentation (70eV EI or high pressure CID) and why $99^+$ is larger when further fragmentation is unlikely (low energy EI or low pressure CID).

In addition to these fragmentations already observed, a number of new transitions not previously reported are observed, such as the McLafferty rearrangement in the short chain and its further fragmentation ($142^+ \rightarrow 114^+$, $114^+ \rightarrow 86^+$, $114^+ \rightarrow 70^+$, $114^+ \rightarrow 58^+$), eleven fragmentations of the methyl-loss ion ($127^+$) which confirm the methyl loss in the short chain, the formation and fragmentation of the hydrogen-loss ion ($142^+ \rightarrow 141^+$ and $141^+ \rightarrow 99^+$, $141^+ \rightarrow 86^+$), the loss of water from the $\alpha$-cleavage ions ($99^+ \rightarrow 81^+$, $71^+ \rightarrow 53^+$, $57^+ \rightarrow 39^+$) and the fragmentation of the resultant hydrocarbon ions. Over 350 fragmentations not previously reported are shown in Figure 1. A number of these are discussed in the sections which follow, together with fragmentations which confirm or contrast with those reported by the IKES study. Discussion of the formation and fragmentation of specific ions appears in the following sections, arranged in order of decreasing m/z. All the transitions discussed can be seen in Figure 2.

## Group A; $142^+$, $141^+$

The CID spectrum of $142^+$ is very similar in appearance to the EI spectrum of the molecule. The same fragments are observed, with the exception of the

isotopic peaks, which are eliminated by the selection of $142^+$. By controlling the collision gas pressure and ion kinetic energy, the relative intensity of the fragment peaks in the CID spectrum can be made to agree almost exactly with that in the normal EI spectrum. The $142^+ \to 141^+$ transition, not seen in the metastable study, is observed in the CID data.

## Group B; $127^+$

The CID data confirm that the $142^+ \to 127^+$ transition is due to $CH_3$ loss from the short chain, as previously indicated by deuterium labelling in the metastable study. Major CID fragments of $127^+$ are due to further loss in the short chain to produce $114^+$ and $99^+$, indicating that the long chain in $127^+$ is still intact. Another fragmentation is the loss of the elements of propanol to form $67^+$, $C_5H_7^+$.

## Group C; $113^+ - 115^+$

The fragmentation of $113^+$ indicates that it is formed by loss of $C_2H_5^{\cdot}$, probably from the long chain of the molecular ion, since both $99^+$ and $86^+$ are missing. Note also the loss of $C_2H_4O$ to form $C_5H_9^+$.

The authors of the metastable study assigned the weak $142^+ \to 114^+$ metastable to the fragmentation process in eqn. (1), based on deuterium labelling.



$$\text{142}^+ \xrightarrow[\text{metastable}]{-C_2H_4} \text{114}^+ \qquad (1)$$
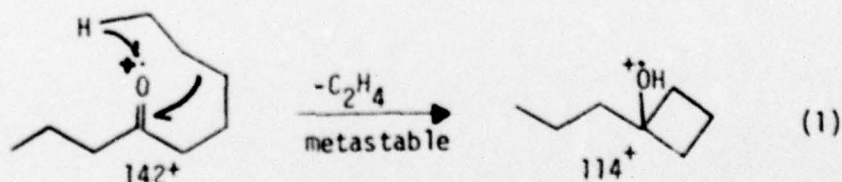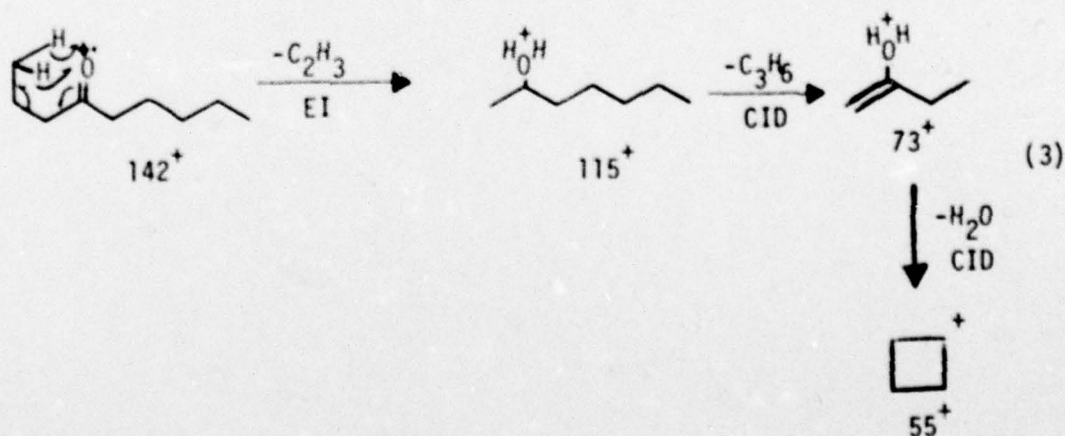
All fragmentations of the $114^+$ ion, however, were attributed to the ion which arises from the McLafferty rearrangement in the short chain as shown in eqn. (2).



$$\text{142}^+ \quad \xrightarrow[\text{EI}]{-C_2H_4} \quad \text{114}^+ \qquad (2)$$
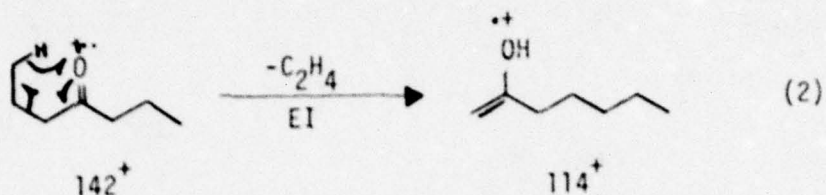
Based on the intense fragment ions of $114^+$ observed at $57^+$ and $58^+$ in this study, the structure of the $114^+$ ion produced by electron impact is that shown in eqn. (2).  It is quite possible that the McLafferty rearrangement which *is observed in EI also occurs by CID.*

The ion at $115^+$ is not an isotopic counterpart of $114^+$ since its fragmentation bears little resemblance to that of $114^+$. The $55^+$ fragment ion is approximately three times as intense as any other ion and could result from the following formation of $115^+$ from a two-hydrogen rearrangement, loss of $C_3H_6$ to form $73^+$, and loss of $H_2O$ to form $55^+$ [eqn. (3)].



$$\text{142}^+ \quad \xrightarrow[\text{EI}]{-C_2H_3} \quad \text{115}^+ \quad \xrightarrow[\text{CID}]{-C_3H_6} \quad \text{73}^+ \qquad (3)$$

$$\downarrow {-H_2O \atop CID}$$

$$\text{55}^+$$

## Group D;   $98^+$-$100^+$

In the study of metastable fragmentation, $99^+$ was observed to be formed from $142^+$ by α-cleavage of the short chain as well as from $114^+$. The CID data show  formation of $99^+$ from $141^+$ and $127^+$ as well. The fragmentation of $99^+$ shows the expected losses, plus the unexpected loss of water to form $81^+$, as shown in eqn.  (4).



$$\text{99}^+ \xrightarrow{} \xrightarrow{-H_2O} \text{81}^+ \tag{4}$$
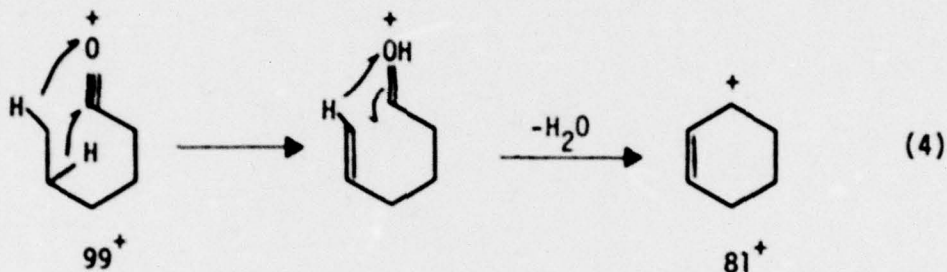
The mechanism of $H_2O$ loss in branched-chain ketones has been elucidated (17), but the very low intensity of the ion due to this loss in straight-chain ketones has precluded its study by deuterium labelling or from experiments involving metastables. Despite the low intensity of the water-loss ion, the CID data make it possible to observe not only the loss of water, but also the further fragmentation of the product ion ($81^+$). Analogous fragmentations which indicate the loss of water are seen for the other α-cleavage ion ($71^+$), as well as for $73^+$, $57^+$, $45^+$, $44^+$, and $31^+$.

The $98^+$ ion is seen as a fragment of $142^+$ in both the CID and metastable studies, with an intensity of approximately 5% of $99^+$. The CID spectrum shows a moderately intense $99^+$→$98^+$ fragmentation, which suggests that the $98^+$ may be formed by a two-step fragmentation from $142^+$ through $99^+$.

## Group E; $81^+$, $85^+$ -$87^+$

The $81^+$ ion does not appear as part of any metastable transition with sufficient intensity to be observed in previous studies. In addition to its formation, as described in Group D above, its fragmentation is clearly observed. The ion series $53^+$, $41^+/39^+$, $29^+$, $14^+$ from the even-electron ion suggests a 6-membered ring.

The formation of $85^+$ from $142^+$ and $114^+$ was noted in metastable studies. We observe that it may also arise from the fragmentation of $100^+$, $99^+$ and $86^+$. The $85^+$ shows the ion series $57^+$, $43^+/41$, $29^+/27^+$, $15^+/14^+$; the absence of a $71^+$ or $70^+$ peak is in agreement with the cyclopentanone structure.

The ion at $m/z$ $86^+$ is formed as expected by the McLafferty rearrangement in the long chain of the molecular ion. Another route for its formation, however, is by loss of $C_2H_4$ from the other McLafferty rearrangement ion, $114^+$. The $87^+$ ion is formed by the "McLafferty +1" rearrangement from the molecular ion. Its fragmentation is quite similar to that of $86^+$ plus a hydrogen, with the exception of the very large $87^+ \rightarrow 45^+$ transition (loss of $C_3H_6$).

## Group F; $67^+$-$73^+$

The $67^+$ ion has not been observed in earlier metastable studies. Its formation was discussed in Group B above. Its fragmentation pattern follows that expected for the even-electron $C_5H_7^+$ ion, and is analagous to the fragmentation of $81^+$ and $53^+$. The $69^+$ and $70^+$ ions also show fragmentation patterns indicative of cyclic alkane ions. The CID spectrum of the even-electron $69^+$ ion shows very good agreement with that of $69^+$ from cyclohexane; the odd-electron $70^+$ ion shows very similar fragmentation to the $70^+$ ion of n-octane.

Two ions are isobaric at $71^+$, $C_5H_{11}^+$ and $C_4H_7O^+$. By careful deuterium labelling in the metastable studies, the $71^+$ ion from $142^+$, $141^+$, $113^+$ and $86^+$ has been shown to be $C_4H_7O^+$; the $71^+$ peak from $99^+$ has been found to correspond to both $C_5H_{11}^+$ and $C_4H_7O^+$. In this CID study, the formation of $71^+$ from all of these ions is observed, as well as the production of $71^+$ from $127^+$, $115^+$, $114^+$, $98^+$ and $87^+$. By consideration of other fragmentations and the neutral losses involved, it is possible to assign the $C_4H_7O^+$ structure for the $71^+$ fragment of $87^+$ (by $87^+\rightarrow86^+\rightarrow71^+$) and $98^+$ (loss of 27). For the other three parent ions ($127^+$, $115^+$, $114^+$) it is not possible to confirm the structure of the $71^+$ fragment based on the available data. Deuterium labelling would aid in these studies.

The fragmentation spectrum of $71^+$ from the EI spectrum of nonan-4-one shows $43^+$ as the most intense fragment, with other fragments at $27^+$, $29^+$, $31^+$ (with intensities 0.40, 0.25 and 0.015 respectively, relative to $43^+$), $15^+$, $39^+$, $41^+$, $53^+$, and $55^+$. For comparison, the CID spectra of $C_4H_7O^+$ from 2-pentanone and $C_5H_{11}^+$ from n-octane were measured under similar experimental conditions. The $C_4H_7O^+$ ion shows the most intense fragment at $43^+$, with other fragments at $27^+$, $29^+$, $31^+$ (intensities 0.40, 0.08, and 0.075 relative to $43^+$), $15^+$, $39^+$, $41^+$, $45^+$ and $53^+$. The $C_5H_{11}^+$ ion produces a CID spectrum with $43^+$ also the most intense fragment, and additional fragments at $27^+$ and $29^+$ (intensities 0.05 and 0.36 relative to $43^+$), $15^+$, $39^+$, $41^+$, $55^+$, and $56^+$. The $71^+$ ion from nonan-4-one shows fragments corresponding to both the possible ions, and is therefore undoubtedly composed of both $C_4H_7O^+$ and $C_5H_{11}^+$. Based on the relative intensities of the $27^+$ and $29^+$ peaks, the contributions to the $71^+$ ion signal are estimated to be 30% $C_5H_{11}^+$ and 70% $C_4H_7O^+$.

The $72^+$ ion yields the fragmentations expected for the addition of H˙ to $71^+$. The major pathways for formation of $72^+$ are "γ-cleavage + 1" from $114^+$ and $87^+$, and McLafferty rearrangement from $100^+$. The formation of $73^+$ from $115^+$ and its fragmentation by loss of $H_2O$ to form $55^+$ was discussed in Group C. Other major fragmentation pathways for $73^+$ are loss of $C_2H_4$ and $C_2H_6$ to form $45^+$ and $43^+$ respectively.

## Group G; $50^+$-$60^+$

The ions at $50^+$, $51^+$, $52^+$, $53^+$, and $54^+$ all show fragmentation spectra that are quite similar to those for the same m/z ions from hydro-carbons such as cyclohexane and n-octane. The $55^+$ ion, however, shows a peak in the CID spectrum at $27^+$ that is 1/3 greater in relative intensity than the $27^+$ ion seen from $55^+$ ($C_4H_7^+$) in reference alkane CID spectra. This may indicate that a small portion of the $55^+$ peak is due to the $C_3H_3O^+$ ion. Although the CID spectrum of $C_3H_3O^+$ has not been measured for reference, the major fragmentation would likely be $55^+ \rightarrow 27^+$, with loss of CO. In the EI mass spectrum of cyclopentanone, the $C_3H_3O^+$ ion comprises 94% of the $55^+$ base peak, and its formation has been carefully studied (11). It is improbable or impossible that $55^+$ formed from $142^+$, $115^+$, $113^+$, $86^+$, $73^+$, $72^+$, $71^+$, ($C_5H_{11}^+$), $70^+$ or $69^+$ would be $C_3H_3O^+$, but it is possible that fragmentation of $127^+$, $99^+$, $98^+$, and $71^+$($C_4H_7O^+$) could produce $C_3H_3O^+$ as well as $C_4H_7^+$.

The peak at m/z $56^+$ can also correspond to two different ions, $C_4H_8^{+\cdot}$ and $C_3H_4O^{+\cdot}$. The fragmentation matches that of $C_4H_8^{+\cdot}$ with the exception of the $28^+$ ion which is more intense than in the reference spectrum. The extra intensity at $28^+$ is undoubtedly due to the $C_2H_4^{+\cdot}$ fragment of $C_3H_4O^{+\cdot}$. Both $C_4H_9^+$ and $C_3H_5O^+$ are possible structures for

the $57^+$ ion. Only the $57^+$ fragment from $85^+$ has been assigned (as $C_3H_5O^+$) based on metastable results. The CID data show that the $86^+$ ion also fragments to form $C_3H_5O^+$, but it is impossible to positively assign without further study either the $C_4H_9^+$ or $C_3H_3O^+$ structure to the other 11 fragmentations observed that lead to $57^+$. The CID spectrum of $57^+$ from nonan-4-one shows a peak at $31^+$ that is not observed in the otherwise similar spectrum of $C_4H_9^+$ from n-octane. The $31^+$ ion probably corresponds to the loss of $C_2H_2$ from $C_3H_5O^+$.

The CID spectrum of the $58^+$ ion shows two major fragments, $43^+$ and $15^+$. The interpretation of the CID spectrum indicates the acetone ion $(CH_3)_2CO^{+\cdot}$; comparison with reference spectra shows it to be identical with those for $(CH_3)_2CO^{+\cdot}$ from acetone and 2-pentanone.

## Group H; $38^+$-$45^+$

The ions at $38^+$, $39^+$, $40^+$, and $41^+$ all show very good agreement with alkane reference CID spectra. The ions at $42^+$, $43^+$, and $44^+$, however, are mixtures of alkane and ketone ions. The $42^+$ ion shows an additional intense fragment at $14^+$ undoubtedly due to the formation of $CH_2^+$ from $CH_2CO^+$.

The reference CID spectra of the two possible $43^+$ ions, $CH_3CO^+$ and $C_3H_7^+$, include all the same ions; the major difference is the ratio of the intensities of the $27^+$ and $15^+$ peaks: approximately 5:1 for $C_3H_7^+$, and 1:20 for $CH_3CO^+$. The $43^+$ peak from nonan-4-one shows fragments at $27^+$ and $15^+$ in the ratio 1:4. Based on these data, the $43^+$ peak corresponds to 75% $CH_3CO^+$, the remainder being $C_3H_7^+$. The $43^+$ peak is quite common in the CID spectra; all but 3 ions above m/z $57^+$ show a $43^+$ peak.

The CID spectrum of $44^+$ shows the fragmentations that would be expected for $CH_3CO^+$ with one $C^{13}$ or an extra H. The $45^+$ ion includes $H_3O^+$ (loss of acetylene) as one of the most intense fragment ions in its CID spectrum.

## Group I; $26^+ - 31^+$

The ions at $26^+$, $27^+$, $28^+$, $29^+$ and $30^+$ all give CID spectra which agree well with the reference CID spectra for hydrocarbon ions. The $31^+$ ion, however, must contain O, and indeed fragment ions are observed at $18^+$ and $(31-18)^+$.

## CONCLUSIONS

The application of the triple quadrupole system to the collision-induced dissociation of the ions of nonan-4-one has identified over 400 fragmentation paths. This enormous increase in the amount of information available for the structure elucidation of the compound compared to that obtained by earlier IKES metastable studies is a result of several features of the triple quadrupole system: 1) The use of CID increases the number of fragmentations that occur, and their intensity. 2) The high sensitivity of the system makes it possible to study transitions of very low intensity. 3) The use of two stages of direct mass analysis eliminates any ambiguity in the identification of parent and daughter ion $m/z$. 4) There is no restriction on the neutral loss. 5) Unit mass resolution is achieved and is unaffected by the kinetic energy loss upon fragmentation.

Interpretation of the CID spectra has made it possible to assign specific structures to a number of the fragment ions of nonan-4-one. Confirmation of these structures can be achieved by comparison of the spectra with reference CID spectra of ions of known structure. In the case of fragment peaks which correspond to two isobaric ions, it is possible to estimate the contribution of each ion by comparison with the reference spectra, without resorting to the high resolution necessary to separate the isobaric ions. The ability

to measure the probability of further fragmentation for the fragment ions which arise from $\alpha$-cleavage has made it possible to explain the apparent preference for $\alpha$-cleavage in the long chain in 70eV EI spectra and for $\alpha$-cleavage in the short chain at 10eV.

A potentially powerful system for structure elucidation of organic compounds should be realized by the combination of complete CID fragmentation data with computer programs which use heuristic or pattern recognition techniques for structure identification. The completeness of the CID fragmentation data and their ability to show relationships among the ions in the mass spectrum should make computer interpretation extremely powerful.

## ACKNOWLEDGEMENTS

## FIGURE CAPTIONS

Figure 1.  Collision-induced fragmentations of nonan-4-one from this study (below the diagonal), metastable fragmentations from previous IKES study (7) (above the diagonal), and EI mass spectrum (along the diagonal).

Figure 2.  Major fragmentations of nonan-4-one observed in both this CID study.  Starred transitions have also been observed in previous mestastable studies (7).
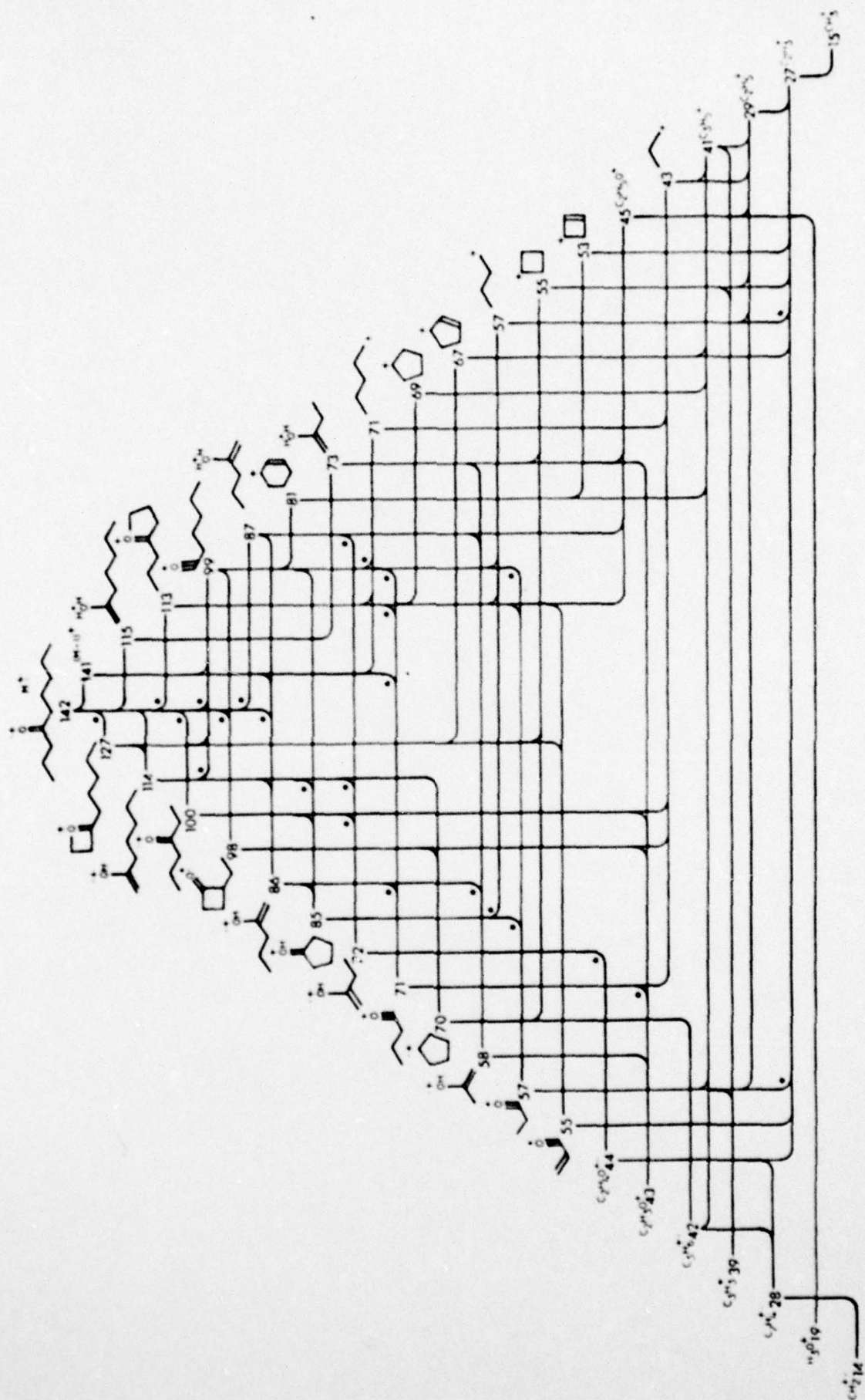
FIG. 1
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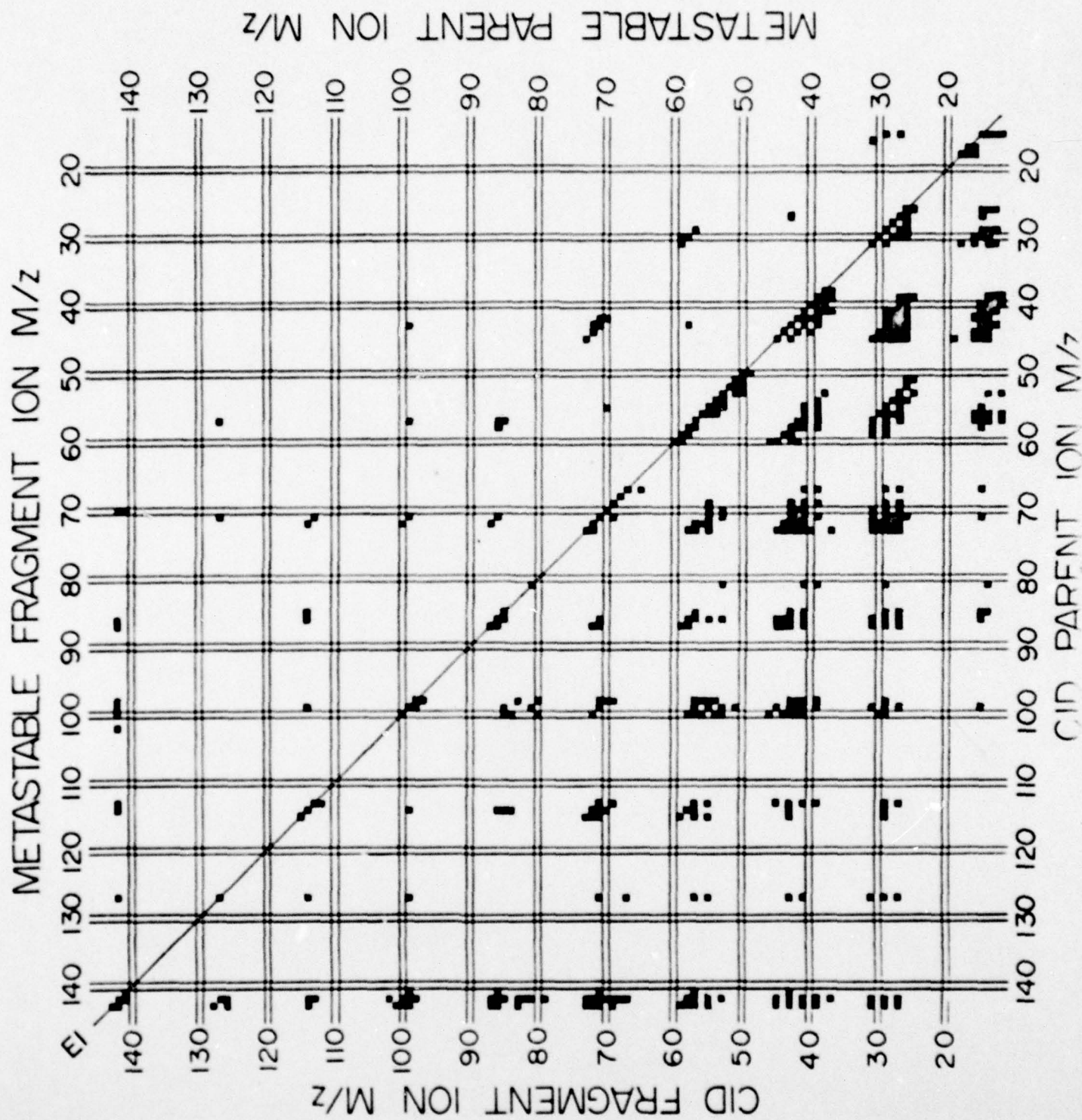
FIG. 2 - Yost, Enke

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